Nano Innovation 2016 Rome, 20-23 September
Conference & Exhibition

ISTITUTO PER I POLIMERI COMPOSITI E BIOMATERIALI

Epoxy Resins and Composites with Self-Healing Ability

Eugenio Amendola
e-mail eugenio.amendola@cnr.it

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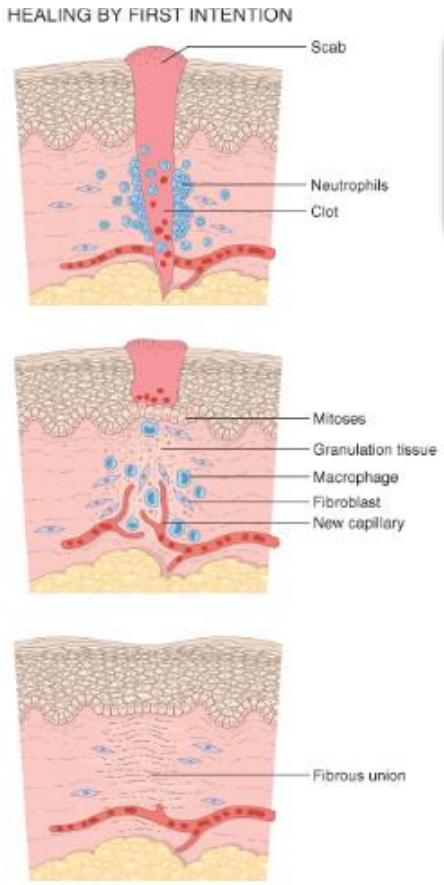
Self-healing materials

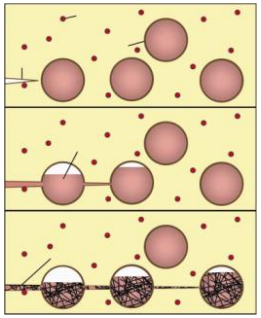
Healing in nature and extrinsic healing

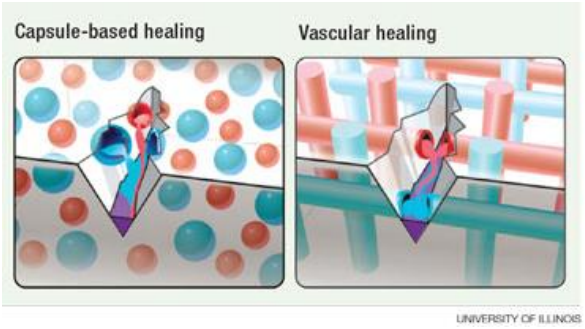


Many natural systems are inherently self-healing. The observation of nature has inspired the concept of functional mendable materials.

Traditional approach

Classical self-healing concepts are based on the embedment of hollow-fibers/microcapsules in the resin.





*Nature **2001**, 409, 794*

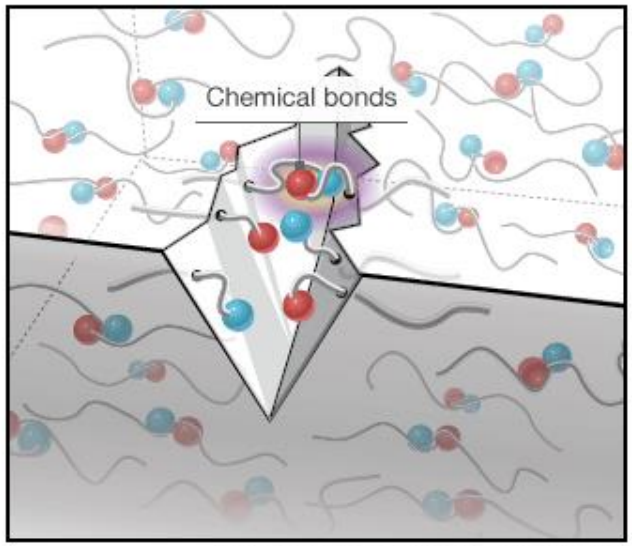
Self-healing materials

Intrinsic healing

A new class of self-healing materials can be obtained by adopting crosslinked polymers, with thermally reversible covalents bonds.

Suitable reactive groups can be produced during fracture and can be repaired by applying a proper thermal stimulus.

Innovative approach



Source: Janet Sinn-Hanlon, Scott White, Ben Blaiszik

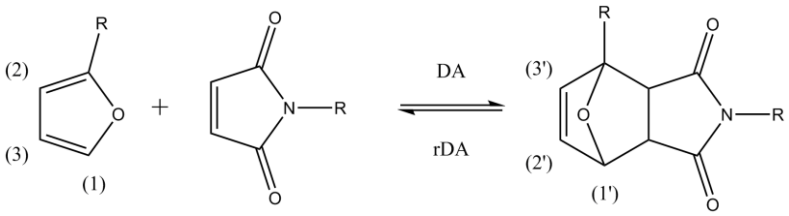
From Scopus database, june 2016.
"epoxy + self-healing"

2016	42
2015	73
2014	83
2013	52
2012	51
2011	48
2010	32

Thermosets with thermally reversible bonds

Research motivation

The most studied thermoreversible systems are based on Diels Alder reaction, because it ensures a high number of recycles.



In the case of Diels-Alder reaction, selection of furan and maleimide fixes the healing temperature in the processing window between 80-90 and 120°C.

Research motivation:

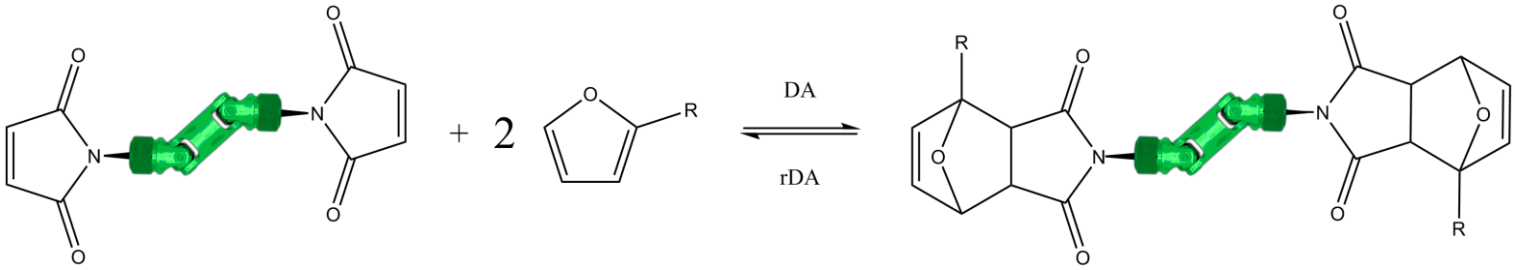
- Methodical investigation of molecular architecture;
- Assesment of self-healing features.

Design of polymeric structures

hybrid architecture

Design of networks with robust healing capabilities is based on hybrid architecture possessing both reverible bonds as well as irreversible ones.

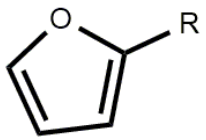
First step: central core

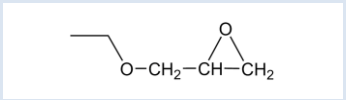
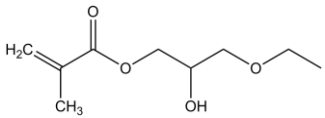
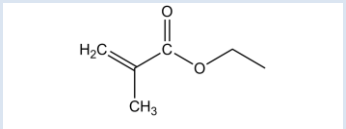
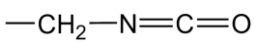
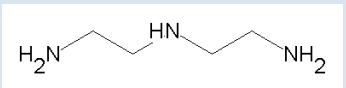


Design of polymeric structures

suitable functional groups

Second step: reactive group



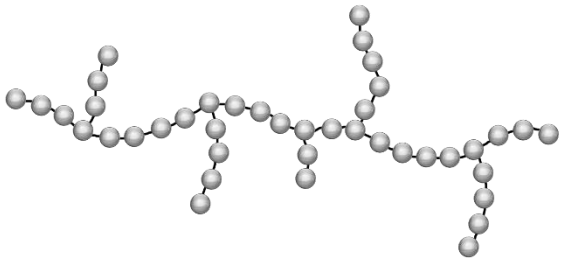
Functional Groups		Network type
ossirane		Epoxy resin, cured with amines or anhydride. Adhesive and structural application.
vinyl ester		Vinyl ester resin. Cured by radical or ionic chain polimerization. Structural and coatings.
acrylate		Acrylate resin. Cured by radical or ionic chain polimerization. Coatings.
isocyanate		Polyurethane resin. Cured with polyols. Coatings and structural.
amine		Crosslinking agent for ossirane or isocyanate

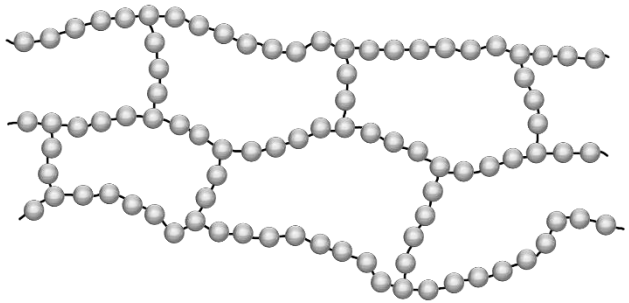
Variable D-A content

Thermosets vs. Thermoplastics

Thermoplastic and thermosetting polymers differs in their 3-D structures.
The following properties are mainly affected:

- thermo-mechanical stability
- glass transition
- melting/solubility



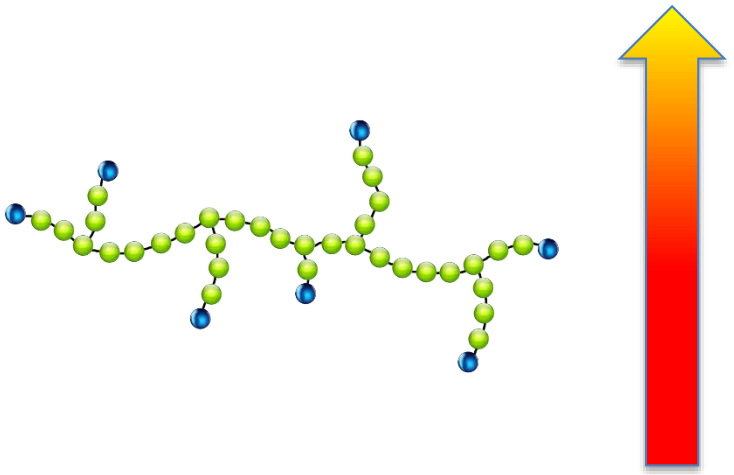


Thermoplastic and thermosetting are considered as DIFFERENT chemical categories

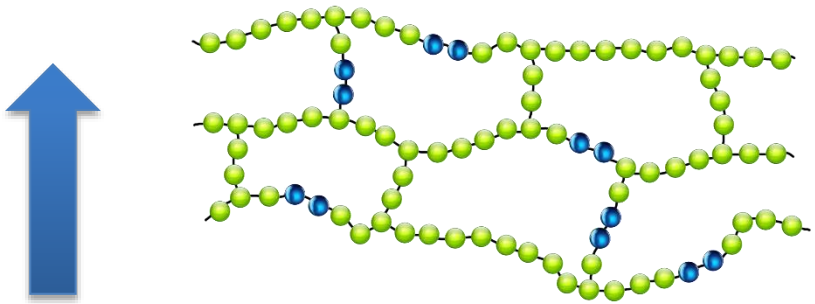
Variable D-A content

Thermosets vs. Thermoplastics

The presence of thermo-reversible covalent bonds (D-A) in the 3-D network induces reversible transormations.



temperature



temperature

External stimulii (heat energy) can trigger the thermomechanical behaviour from thermosetting to thermoplastic and viceversa. Thermally amphoteric features can be identified.

Variable D-A content

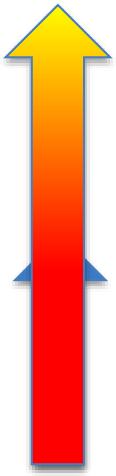
crosslinking density

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i} = \frac{\sum mol_i f_i}{\sum mol_i}$$

Stoichiometrically balanced mixture of:

- bifunctional epoxy
- tetrafunctional amine

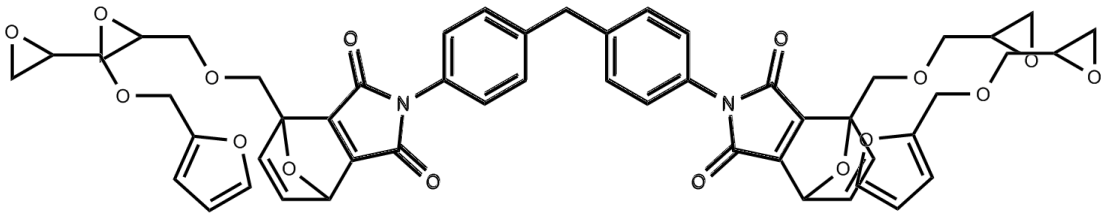
Leads to an f_{avg} = **2.60**



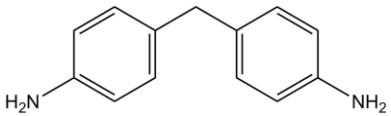
temperature

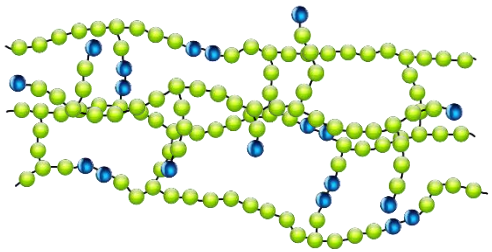
decrease crosslinking density

increase crosslinking density



+

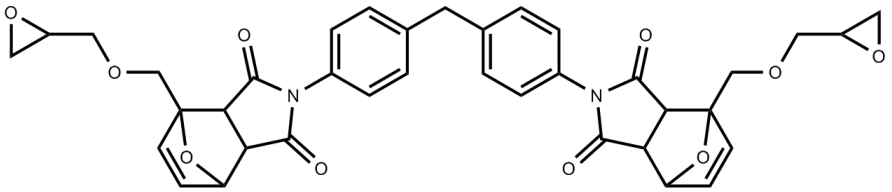




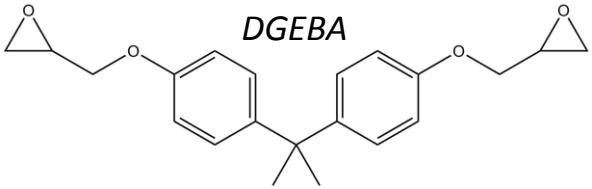
Self healing epoxy resin

all mixture constituents

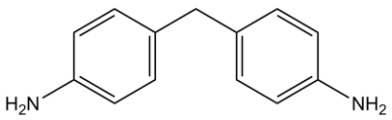
2Ph2Epo



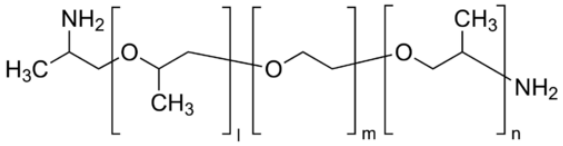
DGEBA



DDM



Jeffamine 500



m ≈ 9

(l+n) ≈ 3.6

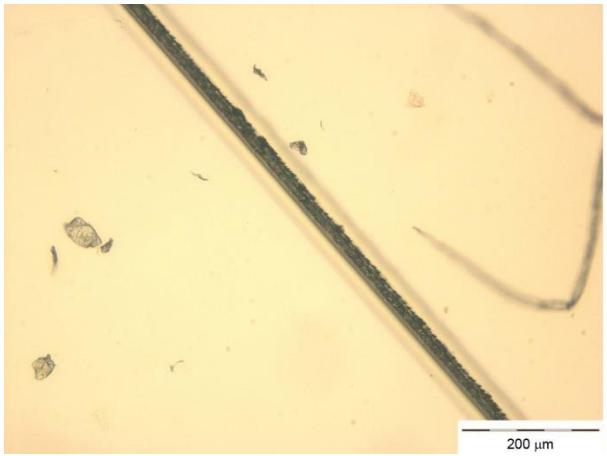
Healing cycle:

I step – high mobility @ 120°C

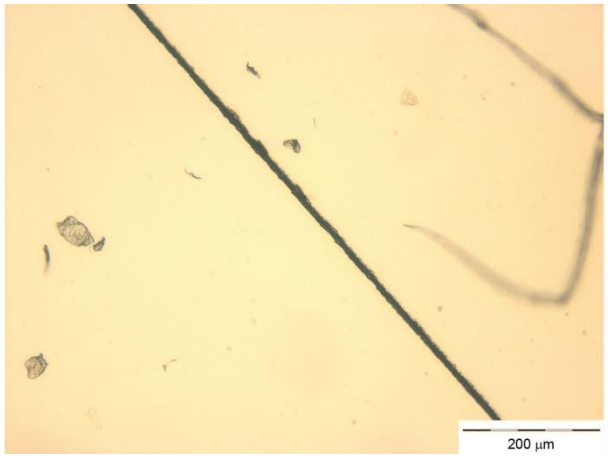
II step – crosslinking recovery – annealing @ 90°C

Scratch damage recovery

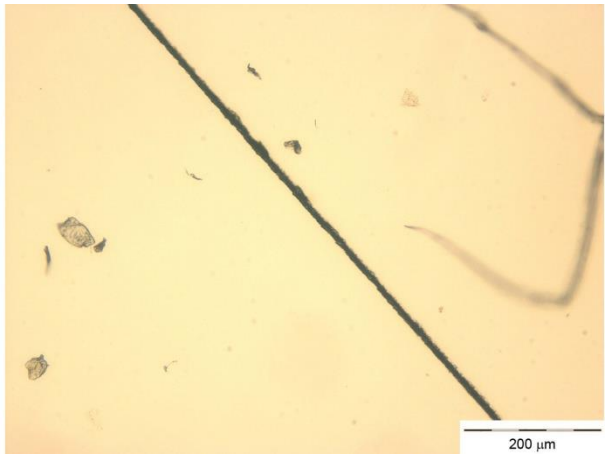
crosslinked DGEBA



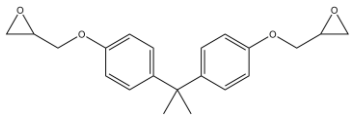
Room temperature



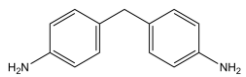
140°C



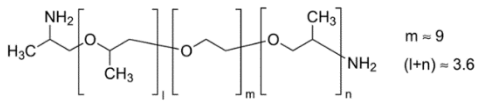
140°C after 20 min



100%



60%



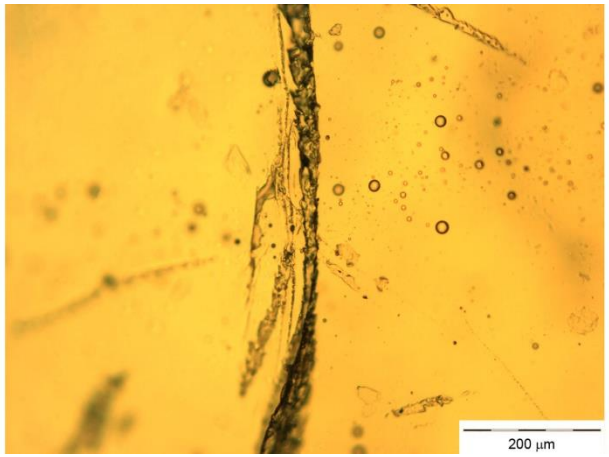
40%

Stable 3-D network prevents material flow and damage recovery.

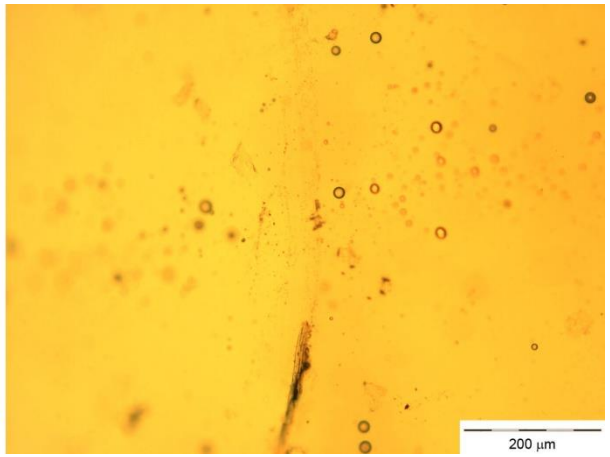
Scratch damage recovery

crosslinked 2Ph2Epo100

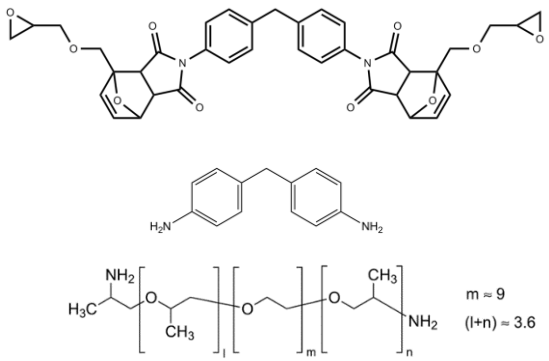
Room temperature



120°C



120°C after 5 min



100%

60%

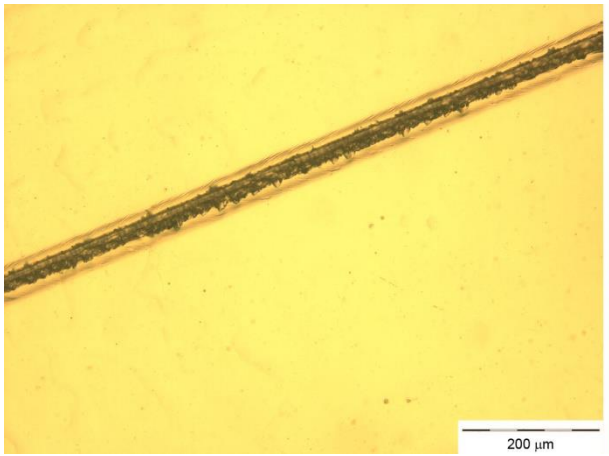
40%

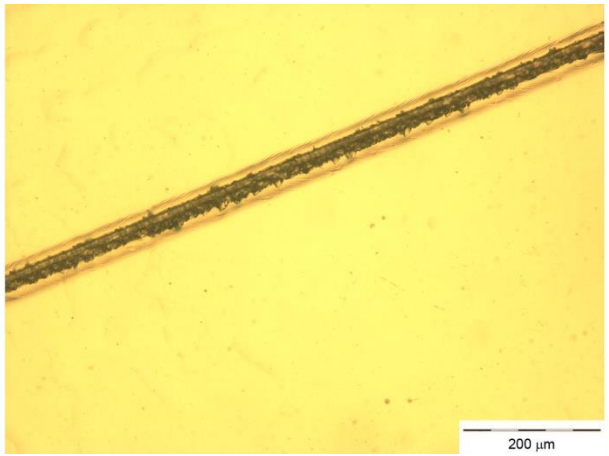
Good morphological damage recovery.

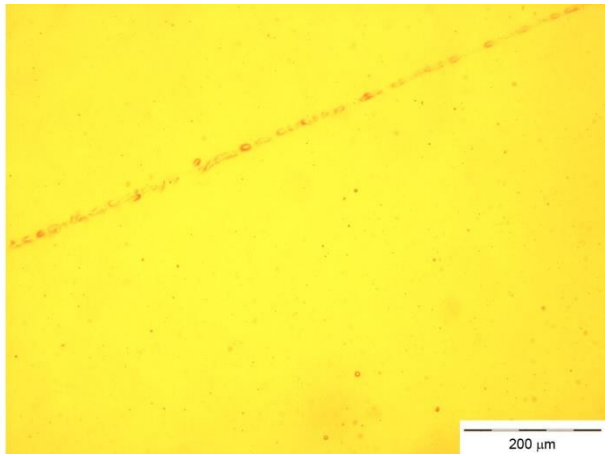
Poor thermo-mechanical stability at 120°C may result in sample deformation and collapse.

Scratch damage recovery

crosslinked 2Ph2Epo65



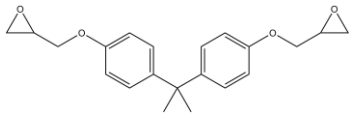




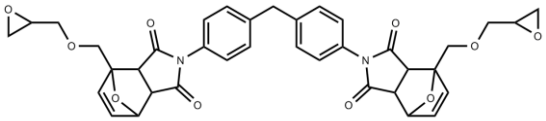
Room temperature

120°C

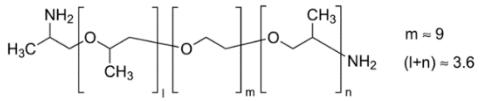
120°C after 30 min



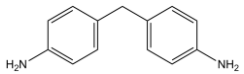
35%



65%



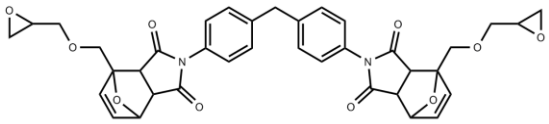
40%



60%

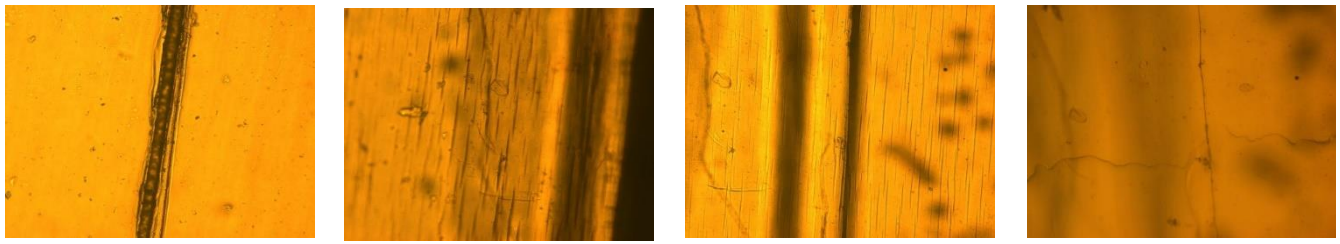
Hybrid network, for improved stability @ high temperature.

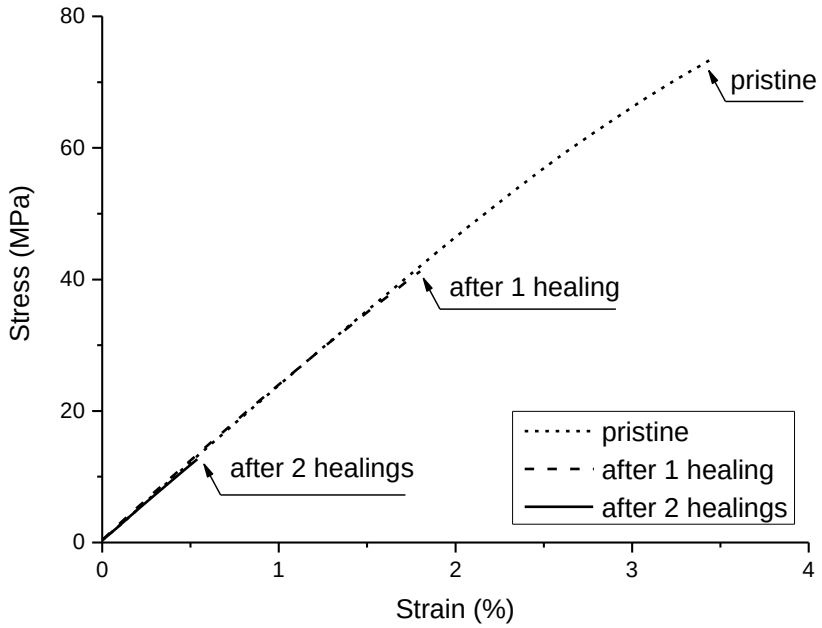
Healing is a compromise, but still working!!!



Fracture recovery

crosslinked 2Ph2Epo65



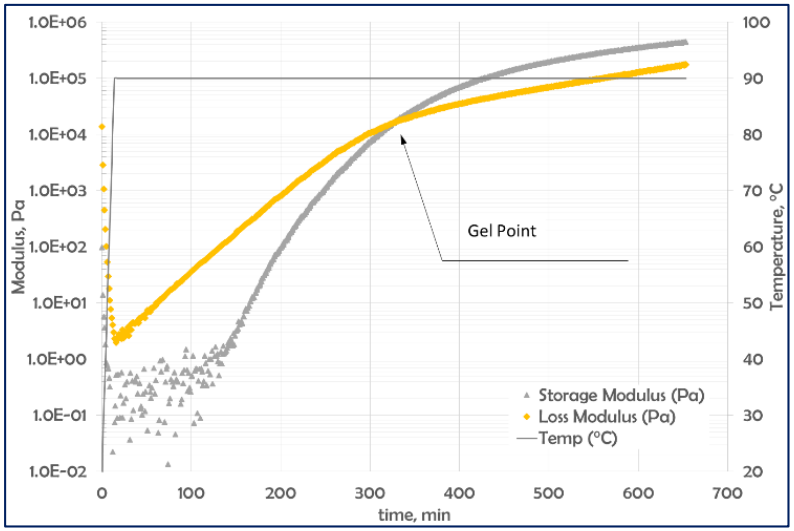


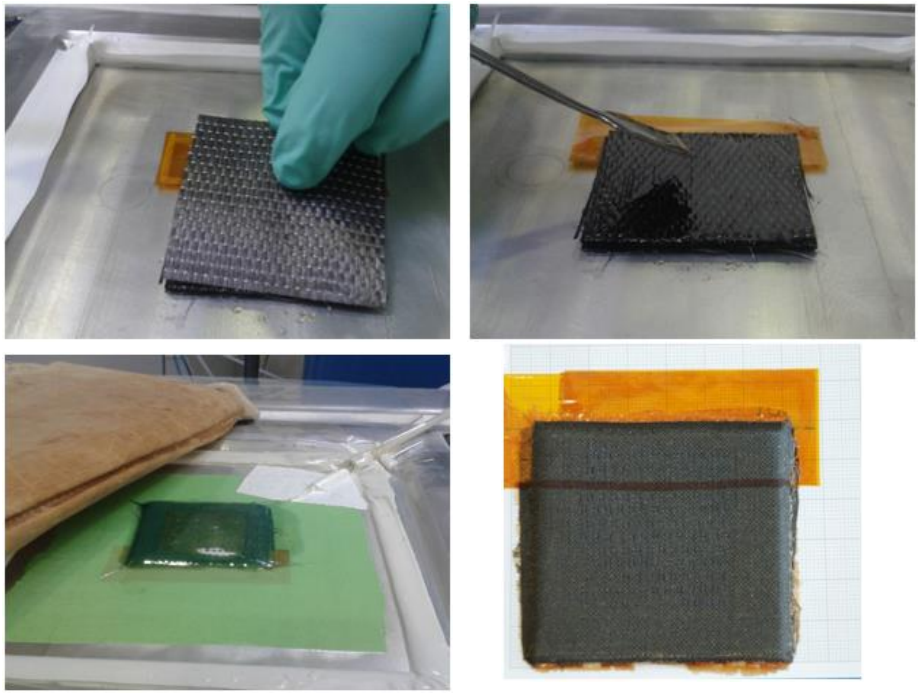
The healing treatment allows a complete recovery of mechanical stiffness (mean value 2.750 GPa) while the failure at break decreases.

Fracture behavior changes from ductile to brittle with increasing healing cycles.

Self-healing composite

Processing





Developed resin can be used according to traditional composite manufacturing processes :

- as matrix in the manufacturing of a small plane laminate (liquid infusion and pre-pregging;

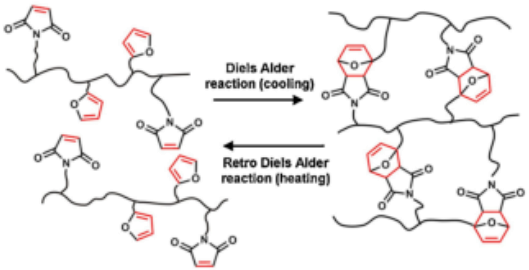
Self-healing composite

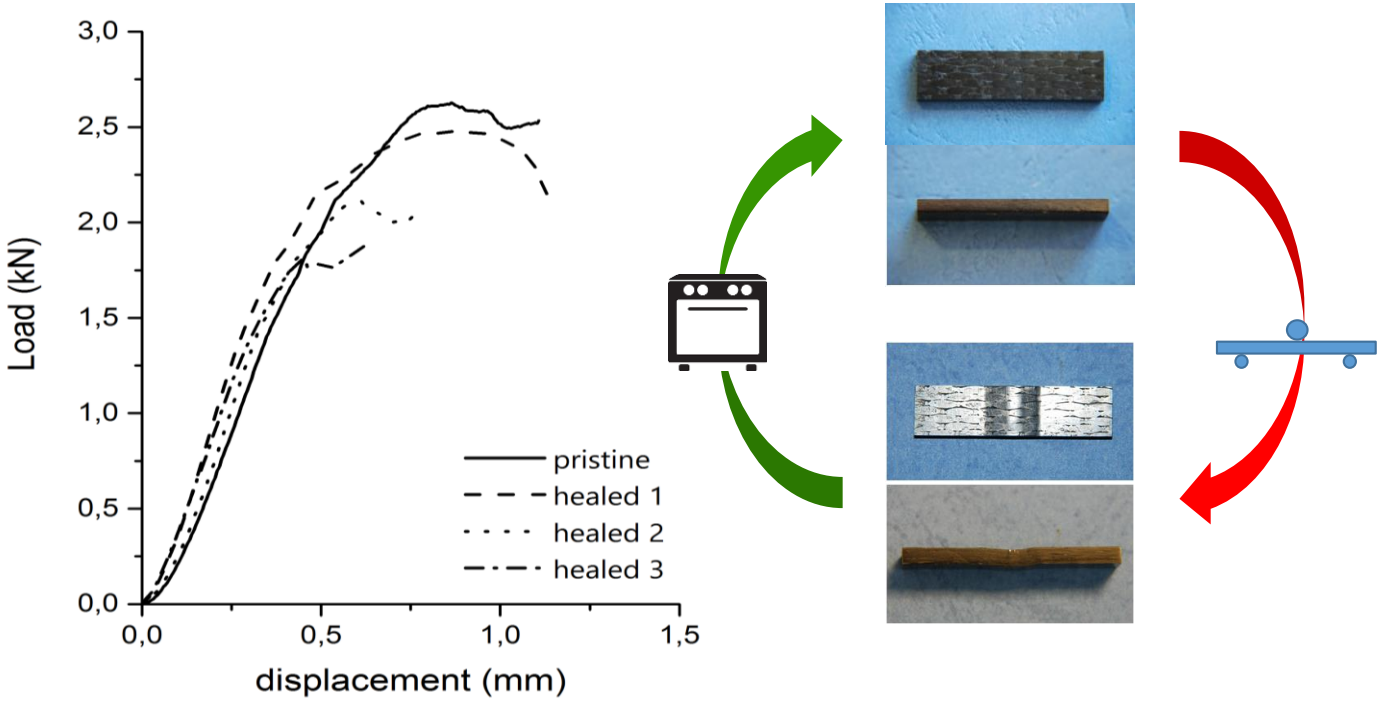
ILSS test

Interlaminar Shear Strength

ASTM D2344

Evolution over 3 consecutive healing cycles

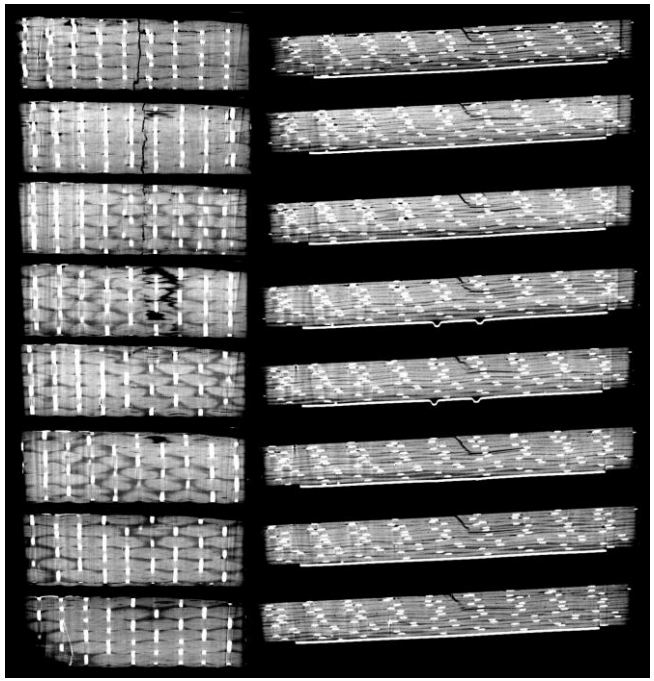




Self-healing composite

NDT analysis CT scan

CT Scan after the last load cycle



Courtesy University of Bath

$$\eta(\%) = \frac{ILSS^{healed}}{ILSS^{pristine}} \cdot 100$$

Healing Cycle	ILSS (Mpa)	Recovery (%)
0	54.1±1.1	100
1	51.4±5.1	95.1
2	44.2±4.9	81.7
3	37.0±5.2	68.4

Conclusions

Part I

Material design

- Synthesis of Diels-Alder epoxy
- Formulation of self-healing epoxy resin
- Composite lay-up

Part II

Self-healing assesment

- Scratch recovery
- Fracture recombination
- Unidirectional carbon fiber composites

Acknoweledgements

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Prof. Alfonso Iadonisi
Dr. Maddalena Giordano

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